ENVIRONMENTAL CHEMISTRY of SELENIUM

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Selenium and Salinity Concerns in the Salton Sea Area of California

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I. BACKGROUND

Selenium concentrations are elevated in subsurface drainwater in the Imperial Valley of California and in surface drains and rivers conveying irrigation drainage (Setmire et al., 1990, 1993). Selenium also is at levels of concern in biota utilizing these resources and in the Salton Sea. The Salton Sea area occupies a topographic and structural trough (Fig. 1). The trough is a landward extension of the depression filled by the Gulf of California, from which it is separated by the broad fan of the Colorado River Delta (Loeltz et al., 1975). The Salton Sea is a closed inland lake occupying about 930 km^2 whose shoreline is currently at an elevation of about 78.3 m below sea level. At its southern end, the Salton Sea is the terminus of the New and Alamo Rivers, which receive irrigation drainwater from a 2250 km drainage network in the Imperial Valley. The New River also receives municipal and industrial waste from the city of Mexicali, Mexico, along with agricultural return from the Mexicali Valley. The Salton Sea National Wildlife Refuge, located in the southern end of the Salton Sea, is a major waterfowl stopover on the Pacific Flyway. At its northern end, the Salton Sea receives agricultural return flow and runoff from the Coachella Valley via the Whitewater River.

The Imperial Valley is typical of a desert area, with a maximum temperature more than 37.8°C more than 110 days per year. Evapotranspiration from a

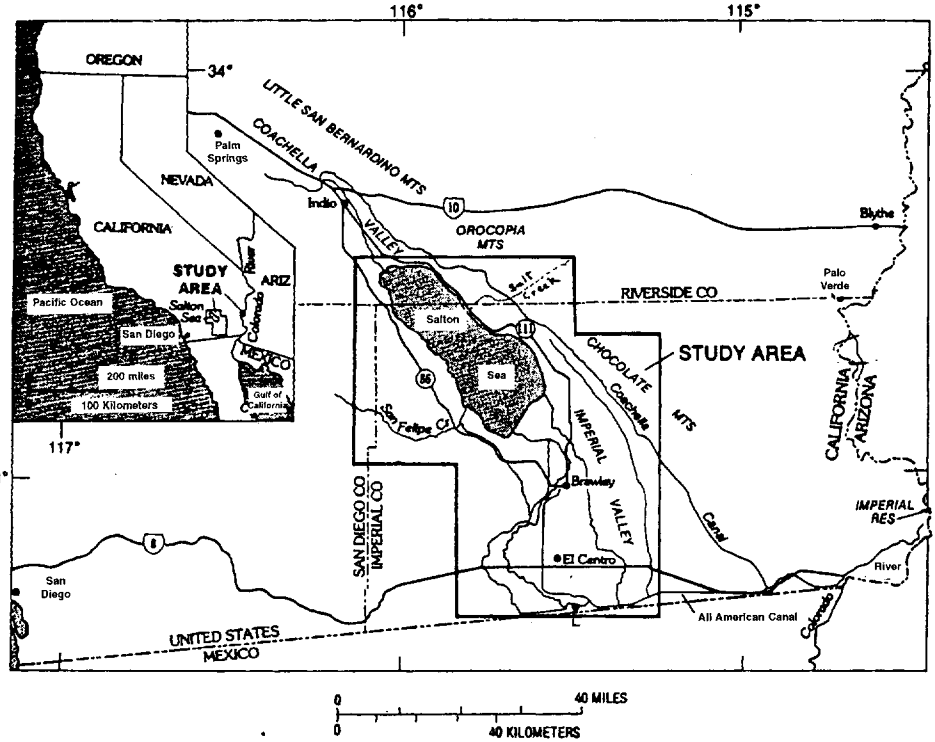

FIGURE 1 Location of study area.

growing crop can exceed 1.80 m/year and during hot summer months exceeds 0.8 cm of water per day. The frost-free period is greater than 300 days for 9 of 10 years and 350 days for 3 of 10 years (Zimmerman, 1981). Imported water has transformed this desert environment into a highly productive agricultural area, permitting the growth of crops year-round.

Colorado River water is diverted at Imperial Dam and delivered via the All-American Canal and a 2700 km network of canals and laterals to 194,717 ha (1995) of farmland in the Imperial Valley. Agriculture and livestock grossed $1 billion in revenue for 1995. Of the agricultural use, field crops totaled 173,406 ha (alfalfa, 75,075 ha; Sudan grass, 31,316 ha; wheat, 25,138 ha; and sugar beets, 12,793 ha), and garden crops totaled 36,471 ha (lettuce, 6800 ha; carrots, 5906 ha). The total land in crops was 218,332 ha, with 32,396 ha having duplicate crops (Imperial Irrigation District, personal communication, 1996).

Water ordered by the farmers is delivered by Imperial Irrigation District to the fields with delivery available to each 65 ha. Irrigation water is accounted for in the following manner. "Operational loss" is the excess water needed to convey the requested water to the field. The excess water is discharged to a surface drain. This loss represents about 15% of the flow in the Alamo River at the outlet to the Salton Sea. Water delivered via the lateral canals is applied to the head of the field using flood irrigation (furrow and border strip) and flows downgradient to the lower or tail end. More water than a crop requires is applied to maintain sufficient wetting time at both ends of the field for effective irrigation. This excess water, commonly called tailwater, is collected at the lower end of the field and discharged to the surface drains. Tailwater is similar in concentrations of total dissolved solids and selenium to Colorado River water used for irrigation, although it has a higher silt load and wash-off of pesticides and nutrients.

Irrigation water infiltrates through the soil. Some of this water is intercepted by shallow tile lines installed at a depth of 2 to 3 m to prevent salt accumulation in the root zone. Spacing of these tile lines depends on the soil type. The distance varies from about 15 m in the northern part of Imperial Valley, where Imperial Formation clays are present to 120 m on the east and west sides of the valley, and to the south where Rositas sands are present (Zimmerman, 1981; Imperial Irrigation District, personal communication, 1989). In clayey soils, water applied to the surface flows more freely through the permeable backfill material used to fill trenches dug for installation of the tile lines than through the adjacent soil. This "trench flow" produces increased flows to the tile drains for a shorter duration than is observed in areas having loamy or sandy soil (Tod and Grismer, 1988). Of the water percolating through the soil, only the water within about 3 m (horizontal distance) of the tile drain is affected. Water at greater distances moves more slowly to the drains, and some of it recharges the aquifer beneath the field. Water in the tile lines is collected and discharged via sumps or gravity tile outlets to the surface drains. This discharge is termed subsurface drainwater or "tile" water. Drainwater is collected by a 2370 km drainage network that discharges either to the New River or the Alamo River, or directly to the Salton Sea.

In 1986 irrigation drainwater studies began in the Salton Sea area as part of the National Irrigation Water Quality Program (NIWQP) of the Department of Interior. The NIWQP originated as an outgrowth of the concern over the selenium contamination problems at Kesterson Reservoir, California. Other irrigation drainage projects in the western United States that had the potential for selenium contamination were investigated. Investigations into selenium contamination problems in the Salton Sea and planning studies for selenium remediation are ongoing to date (1997).

II. EFFECT OF IRRIGATED AGRICULTURE ON WATER QUALITY

A. Irrigation Water

Colorado River water is used to irrigate crops in the Imperial Valley. The quality of this irrigation water varies yearly as natural events (floods and droughts) and anthropogenic factors (land development and management, including irrigation activities) control the quality of water in the Colorado River. Water in the East Highline Canal (Colorado River water) was sampled monthly from August 1988 to August 1989. The median dissolved solids concentration was 686 mg/L, with a selenium concentration of 2 μg/L, and a Se/Cl ratio of 2.2×10^{-5} (Setmire et al., 1993). Hydrogen and oxygen isotopes and tritium concentrations were analyzed in one water sample. Concentrations were the following: δD (deuterium) = -103 permil, δ^{18}O (Oxygen) = -13 permil, and tritium concentration = 30 tritium units (TU) (Schroeder et al., 1993). These concentrations and ratios will be used in Section II.C later as a reference to show changes that occur as water moves through the agricultural system in the Imperial Valley. The Se/Cl ratio will show relative sources and sinks of selenium, the hydrogen and oxygen isotopes will show the evaporative history of the water, and the tritium will show the relative composite age of the water.

B. Surface Drainwater

Surface drainwater in the Imperial Valley is found in the 2250 km network of drains, in the New and Alamo Rivers, and in the Salton Sea. The Alamo River consists almost entirely of surface drainwater. The median selenium concentration for monthly water samples collected from the Alamo River at its outlet to the Salton Sea during August 1988 to August 1989 was 8 μg/L, and the median dissolved solids concentration was 2170 mg/L (Setmire et al., 1993). Total water discharge in the Alamo River for the sampling period was 74,100 hectare-meters (ha · m), yielding a total selenium load of 5.9 metric tons discharged to the Salton Sea. In comparison, the New River contributed only 2.3 metric tons of selenium for the same sampling period. Both water discharge and selenium concentrations were lower for the New River.

Surface drainwater is composed of subsurface drainwater, operational loss, canal seepage, tailwater runoff, and occasionally storm water. These sources can be divided into two categories: the first category is subsurface drainwater; the second category incorporates the remaining components of surface water that have major ion and selenium concentrations similar to the Colorado River (Setmire et al., 1993, Michel and Schroeder, 1994) and are referred to as dilution water. Median concentrations from the 1988–1989 monthly sampling performed by the U.S. Geological Survey (USGS) can be used in a simple two-component mixing equation to calculate the percentage composition of water in the Alamo River at its outlet to the Salton Sea. The two components are described above: subsurface drainwater and dilution water. The water in the Alamo River and/or in surface drains is the result of that mixing.

The equation is:

$$X A + (1 - X) B = C$$

where A = concentration of Colorado River water (dilution water), B = concentration of subsurface drainwater, and C = concentration in Alamo River at the outlet (also of surface drains).

For chloride the equation is:

$$X(92 \text{ mg/L}) + (1 - X)(1200 \text{ mg/L}) = 420 \text{ mg/L}$$

Solving the equation, the fraction $X = 0.70$. In the Alamo River, 70% of the chloride in the water comes from "dilution water" and 30% comes from subsurface drainwater, while 15% of the chloride comes from dilution water and 85% comes from subsurface drainwater. Solving the equation using median concentrations for dissolved solids yields a value for dilution water (x) of 77%. These values show that about three-fourths of the water in the Alamo River comes from "dilution water" and about one-fourth from subsurface drainwater.

Concentrations in water change rapidly as subsurface drainwater is discharged to the drains and as tailwater and/or operational loss is discharged. Bottom sediment also is affected by these changes. Selenium concentrations in the water column were not good predictors of selenium concentrations in bottom sediments. Rapid changes in the flow rate can resuspend previously deposited material, or deposition can occur as flow velocities in the drain decrease. Either case will produce variable selenium concentrations in bottom sediment. According to Salomons and Forstner (1984), dissolved metal concentrations are partly controlled by the interactions between metals and particulates. Adsorption is a key factor in the removal of trace metals from hydrologic systems. The particle size of the bottom sediment is a major factor controlling metal adsorption. As grain size decreases, metal concentration increases (Horowitz, 1991). Selenium concentrations in bottom sediment were compared with the percentage of bed material finer than 0.062 mm (silt and clay) at about 50 sites from 18 drains to determine whether selenium predominantly occurs on fine sediment (Setmire, unpublished data, 1994). Figure 2 shows that bottom sediment samples consisting mostly of fine material generally have higher selenium concentrations ($r^2 = 0.55$). The bottom sediment sample having the highest selenium concentration of 1.7 μg/g also has the highest portion finer than 0.062 mm at 98%.

Selenium concentrations in 260 soil samples from 15 fields (Schroeder et al., 1993) were compared with selenium concentrations in 48 bottom sediment samples to determine whether selenium concentrations in bottom sediments mirror selenium concentrations in the soil. The median selenium concentration from the soil samples is 0.2 μg/g compared with 0.5 μg/g for the bottom sediment samples. Results of t-tests suggest a very low probability that the two data sets represent the same population. The median concentrations show more than a doubling in selenium concentration from the field soils to bottom sediment in the drains. This increase in selenium concentration in the drain bottom sediments is accompanied by a decrease in the ratio of Se to Cl in the water. The Se/Cl ratio is 2.2×10^{-5} in irrigation water, 2.0×10^{-5} in subsurface drainwater, and

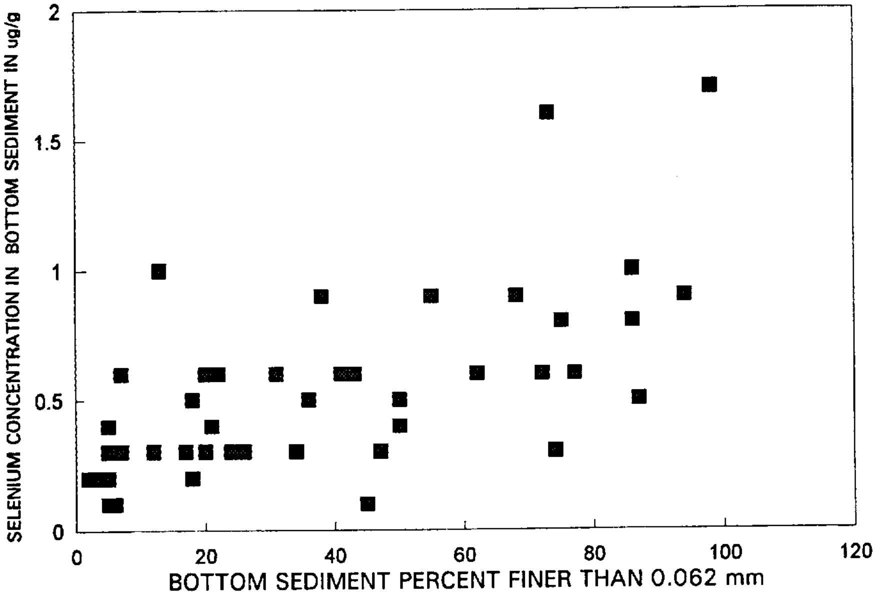

FIGURE 2 Regression plot of selenium concentration in bottom sediment and bottom sediment percentage finer than 0.062 mm for bottom sediment samples collected from selected surface drains in the Imperial Valley, California, August 1994.

1.5×10^{-5} in surface drainwater. Compared with chloride, it appears that some selenium is lost to the drain sediments. Furthermore, it is likely that some selenium reduction is occurring in the drains. Selenium speciation analysis for one drainwater sample showed that selenite comprised 1.4 μg/L of a total selenium concentration of 3.31 μg/L (A. Maest, personal communication, 1989). The effects of reducing conditions have been observed in numerous drains throughout the Imperial Valley. These effects include the presence of black sediment and the generation of hydrogen sulfide gas. Reduction of sulfate to hydrogen sulfide shows that conditions are present whereby selenate also could be reduced. Reduced species of selenium, including selenite, can adsorb on finer sediments that settle, increasing the selenium concentration in bottom sediments.

C. Subsurface Drainwater

Selenium concentrations in 119 sumps or gravity tile outlets sampled during May 1988 ranged from 3 to 300 μg/L, with a median concentration of 24 μg/L and a standard deviation of 58 μg/L (Setmire et al., 1993), reflecting results heavily skewed toward low concentrations. The same sites were sampled in 1986 by the California Regional Water Quality Control Board. Regressions suggest that selenium concentrations were about the same in 1988 and in 1986 ($r^2 = 0.787$, $a < 0.01$, slope = 0.966). The lack of change in concentration confirms that processes controlling selenium concentrations in subsurface drainwater are uniform over long periods. The similarity in concentrations was expected, given the comparative constancy in the source water quality (Colorado River) and the long transit times through the delivery and drainage system.

During August 1994 through January 1995, 820 sumps and gravity tile outlets were sampled for specific conductance and discharge, and 304 water samples were collected to determine selenium concentrations. Selenium concentrations ranged from 1 to 311 μg/L, with a median of 28 μg/L and a standard deviation of 52 μg/L. There was no regression analysis between these data and the 1986 and 1988 data because not all the same sites were sampled. All three sets of data show an area of high selenium and dissolved solids concentrations southeast of the Salton Sea National Wildlife Refuge where land surface altitudes are among the lowest in the Imperial Valley.

Dissolved solids concentrations and specific conductance measurements show a distribution similar to that of selenium, except in the area immediately bordering the southern end of the Salton Sea, where reducing conditions are believed to result in selenium removal. The correlation between specific conductance and selenium concentration for the 1988 data ($r^2 = 0.77$, $a = 0.01$) (Setmire et al., 1993) is about the same as the correlation between dissolved solids and selenium concentrations for the 1986 data ($r^2 = 0.704$) (California Regional Water Quality Control Board, personal communication, 1986). However, the correlation between selenium and dissolved solids concentrations for the 1994–1995 data is only $r^2 = 0.28$ ($a = 0.01$). Sites for the 1994–1995 samples were selected to represent specific areas and as such caused tighter clustering of the data and weakening the correlation between selenium and dissolved solids.

Hydrogen and oxygen isotopes and tritium concentrations were analyzed from subsurface drainwater samples to show the source of the water and the processes affecting its concentration. Hydrogen and oxygen isotopes, which are chemically conservative, provide the ability to distinguish between increases in dissolved solids concentrations owing to leaching without evaporation and increases in dissolved solids owing to evaporation (Fontes, 1980). Evaporation in an arid environment such as the Imperial Valley results in enrichment of the heavier isotopes in the water that remains. Deuterium and oxygen-18 (^{18}O) are enriched in relation to the common forms or hydrogen (^{1}H) and oxygen (^{16}O). Values are reported as δD and $\delta^{18}O$ relative to the Vienna Standard for mean ocean water (V-SMOW).

For subsurface drainwater in the Imperial Valley, $\delta D = 5.4\ \delta^{18}O - 34$ (Fig. 3). The standard error of the slope is 0.16 (Schroeder et al., 1991). Fontes (1980) found that $\delta D = 5.8\ \delta^{18}O - 21$ for irrigation drainage wells in the Juarez

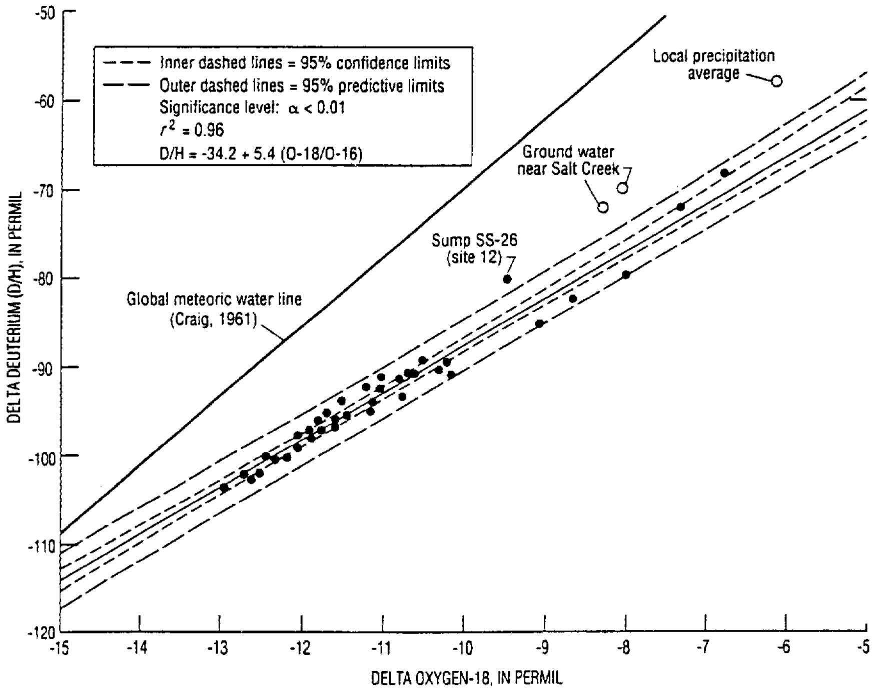

FIGURE 3 Regression plot of hydrogen and oxygen isotope ratios and the global meteoric water line for subsurface drainwater samples collected in the Imperial Valley, California, May 1988.

Valley of Mexico, where the range in dissolved solids concentration was controlled by evaporative concentration as indicated by the global meteoric water line in Figure 3. The comparability of the two slopes, 5.8 and 5.4, shows that similar evaporative processes control the range in dissolved solids concentration in subsurface drainwater from the Imperial Valley. The r^2 of 0.96, $a < 0.01$ (Setmire et al., 1993), suggests a single source of the subsurface drainwater. As indicated earlier, Colorado River water in the East Highline Canal used to irrigate the Imperial Valley has a δD of about -103 permil and a $\delta^{18}O$ of about -13 permil (Schroeder et al., 1993). The regression line showing the relation between hydrogen and oxygen isotopes for Imperial Valley drainwater passes through that point at the lower end and through the isotopic composition of Salton Sea water when extrapolated on the upper end. Therefore, the Colorado River is the source of all subsurface drainwater and surface water in the Imperial Valley, including the water in the Salton Sea. Points not plotting on the regression line lie outside the Imperial Valley or are influenced by water from external sources such as San Felipe Creek, Salt Creek, or local precipitation.

The median tritium concentration in pore water collected at a depth of 1 m near drains in six fields was 32 TU, slightly higher than the tritium concentration in recently analyzed Colorado River water. Tritium concentrations of samples from a depth of 2 m, near the depth of the tile lines, have a median concentration of 52 TU, indicating water with an average transit time of about 5 years (Michel and Schroeder, 1994).

Evaporative concentration of Colorado River water controls the range of dissolved solids concentration in subsurface drainwater from the Imperial Valley (Setmire et al., 1993). U.S. Geological Survey scientists hypothesized that evaporative concentration also controls the range of selenium concentrations. In other areas, such as the San Joaquin Valley of California, oxidation of reduced seleniferous deposits and evaporative concentration produce high levels of selenium in drainwater (Deverel and Fujii, 1987). Data from 270 soil cores collected from 15 fields show that the soil is not a major source of selenium in the Imperial Valley (Schroeder et al., 1993). Regression of δD against selenium initially had a low correlation. Six sites draining fields in a narrow band along the southern end of the Salton Sea strongly affected the regression. These fields had high chloride and low selenium concentrations similar to the Salton Sea and had comparatively reducing conditions. They are atypical of the remainder of the Imperial Valley and were deleted from the regression, giving $r^2 = 0.62$. Similarly high correlations result from regressions between δD and chloride concentrations, δD and dissolved-solids concentrations, and selenium and chloride concentrations. The high correlation between these variables shows that selenium concentrations in subsurface drainwater are controlled by evaporation of Colorado River water.

Selenium is compared with other elements such as chloride to show relative changes that occur as water moves through the agricultural system. These elemental mass (weight) ratios show sources and sinks for selenium. Chloride is used for comparison because it is chemically conservative and highly soluble. Colorado River water in the East Highline Canal had a selenium to chloride ratio (Se/Cl) of 2.2×10^{-5}. This ratio changes when one or the other ion is affected by physical processes, solubility, oxidation–reduction reactions, and/or biological reactions. In the Imperial Valley, the physical process of evaporation affects both elements similarly. The median Se/Cl ratio for subsurface drainwater sampled during May 1988 is 2×10^{-5}. The minimum ratio is 0.027×10^{-5}, the maximum ratio is 7.3×10^{-5}, and 50% of the ratios fall between 1.0 and 3.0×10^{-5} (Setmire et al., 1993). Also, one of the highest detected selenium concentrations, 340 μg/L, had an associated chloride concentration of 15,000 mg/L and a Se/Cl ratio of 2.3×10^{-5}. The similarity of this Se/Cl ratio with the ratio for Colorado River water (East Highline Canal) shows that evaporative concentration of irrigation water is the most important process producing the elevated levels of selenium present in the Imperial Valley.

Crop type and soil characteristics defining where different crops are grown control the amount of evaporative concentration that occurs in a field. For example, Bermuda grass tends to be grown in clayey, more saline soils of lower permeability, while higher value crops, such as lettuce, tend to be grown in more permeable soils (S. Knell, personal communication, 1997). Hence, the soils and crop type affect conductance and selenium in the subsurface drainage from the respective fields. The regression equation describing the relationship between specific conductance and selenium concentration (r^2 =0 .28) for the 304 water samples was used to estimate selenium concentrations from specific conductance values measured during August 1994 through January 1995 at 820 gravity tile outlets and sumps for which crop type was also known. The median modeled selenium concentration for the 820 sites of 36 μg/L is slightly higher than the median of 28 μg/L for the 304 water samples on which selenium was measured. Modeled selenium concentrations ranged from a low of 28 μg/L for fields where lettuce is grown to a high of 52 μg/L for fields where Bermuda grass is grown (Table 1).

D. Quality Changes During Water Transport

Concentrations of several key constituents in Colorado River water are compared with concentrations in surface and subsurface drainwater to show the overall

TABLE 1 Modeled Selenium Concentrations for Selected Crops[a] from Selenium to Specific Conductance Regression for Subsurface/Drainwater Samples Collected in the Imperial Valley, California, August 1994 to January 1995

Crop	Measured selenium (μg/L) Min	Max	*n*	Measured conductance (μS/cm) Min	Max	*n*	Modeled selenium median (μg/L)
Asparagus	13	27	(5)	2,750	37.600	(13)	29
Beds and rows	11	284	(8)	1,970	28,500	(62)	36
Between crops	1	10.5	(4)	4,450	34,000	(16)	40
Bermuda grass	1	167	(29)	1,310	35,500	(80)	52
Disked	2	311	(17)	2,010	24,400	(32)	34
Fallow	5	311	(46)	2,090	42,300	(73)	37
Lettuce	5	31	(5)	2,210	15,950	(26)	28
Sudan	3	50.5	(32)	1,080	22,010	(62)	42
Sugar beets	5	173	(10)	4,540	22,500	(41)	46

[a]*n* = number of sites or samples.

water quality changes due to irrigated agriculture. Median concentrations for monthly samples collected in the East Highline Canal from August 1988 to August 1989 along with concentrations of selected constituents in subsurface water and surface drainwater are shown in Table 2. Concentrations of these selected constituents increase from Colorado River water to irrigation drainwater. Total dissolved solids increases about 3-fold from the source (Colorado River) to output (surface drainwater), nitrate about 20-fold (reflecting use of fertilizers), chloride 4.5-fold, and selenium 3-fold. Some dilution of subsurface drainwater then occurs when fresher water is mixed in the surface drains.

E. Salton Sea

The Salton Sea is the terminus for irrigation drainage originating in the Coachella Valley, the Imperial Valley, and the Mexicali Valley. The Se/Cl ratio in the Salton Sea is 0.007×10^{-5}, showing that the Salton Sea is a major sink for selenium. Evaporation is the major physical process controlling the major ion chemistry of the Salton Sea. Median chloride concentrations increase from 520 mg/L in the Alamo River to about 15,000 mg/L in the Salton Sea. In contrast, median selenium concentrations decrease from 8 μg/L in the Alamo River to 1 μg/L in the Salton Sea (Setmire et al., 1993). Selenium is biologically reduced, eventually ending up in the bottom sediment and the biomass of the Salton Sea, or in the wildlife feeding in the Salton Sea.

A narrow zone of mixing is present between high-salinity Salton Sea water and low-salinity Alamo River water. The Alamo River extends about 500 m into the southern end of the Salton Sea. The river, with levees on both sides, is dredged as needed to maintain adequate flow to the Salton Sea. The mixing zone occurs about 60 m past the end of the levee. The specific conductance in the mixing zone at a depth of 0.4 m was 5000 μS and 51,000 μS at a depth of 1 m (bottom). The selenium concentration was 8 μg/L at the upper depth and only 1.0 μg/L at the lower depth. Samples collected to determine speciation indicate that selenium in the Alamo River, on the river side of the interface, is a

TABLE 2 Median Concentrations of Selected Constituents in Water Samples Representing the East Highline Canal, Subsurface Drainwater, and Surface Drainwater in the Imperial Valley, California

Site	Dissolved solids (mg/L)	Nitrogen (mg/L)		Chloride (mg/L)	Selenium (μg/L)
		As NO_3	As NH_4		
East Highline Canal	686	0.22	0.03	98	2
Subsurface drainwater	6448	1.1	0.07	1200	28
Surface drainwater	2025	4.95	0.19	420	6

mixture of selenate and selenite. The total selenium concentration measured at this site on June 1989 was 6.35 μg/L, with 2.56 μg/L as selenite and 3.79 μg/L as selenate (A. Maest, personal communication, 1989). These concentrations, along with those from the surface drains, show that selenium in the Alamo River flowing into the Salton Sea is fairly evenly divided between the intermediate (+4)(selenite) and the oxidized (+6)(selenate) oxidation states. Samples collected at the seaside of the interface show that for a total selenium concentration of less than 2.4 μg/L (method- specific reporting limit for June 1989 sample), 1.79 μg/L was as Se(+4) and less than 0.2 μg/L as Se(+6). These results show that virtually none of the selenium on the Salton Sea side of the interface is in the (+6) oxidation state (A. Maest, personal communication, 1989).

Selenium concentrations in bottom sediments of the Alamo River delta ranged from 0.2 to 2.5 mg/kg, with no readily apparent spatial pattern in their distribution. A composite sample collected during 1986 contained a selenium concentration of 3.3 mg/kg and had a dissolved organic content of 1%. A sediment core collected in 1996 near the south buoy (deepest location in the Salton Sea) had a selenium concentration of 9.3 mg/kg and a corresponding dissolved organic carbon content of 9.2 percent (R. Schroeder, unpublished data, 1996). This core was composed of very low density material. The high selenium concentration and the high dissolved organic carbon content of this sample show that selenium is likely incorporated into biomass, which degrades and concentrates in the deepest parts of the Salton Sea.

F. Groundwater

Groundwater in the central part of the Imperial Valley is much too saline for consumption, although there has been limited use in isolated areas for domestic livestock. Analyses from shallow monitoring wells from the early 1960s (Loeltz et al., 1975) indicated the presence of some freshwater which, based on the well's location near rivers or unlined canals, probably results from seepage (Michel and Schroeder, 1994). Multidepth piezometer wells installed at three locations in the Imperial Valley showed that regional groundwater is free of influence from irrigation drainage (Setmire et al., 1993). This water has a salinity at about 15 g/L, about one-third the salinity of the Salton Sea. The shallow groundwater system consists of two zones—an upper zone, extending no deeper than about 10 m, and a lower zone that predates the development of irrigated agriculture. The upper zone, produced by infiltrating irrigation drainwater, has highly variable salinity and selenium concentrations. The lower zone is of relatively constant salinity and contains no selenium. The selenium is believed to have been removed by microbial reduction. Environmental conditions, which are toxic near the surface, become increasingly reducing at depth, resulting in several other characteristic geochemical changes as well—removal of nitrate by denitrification, generation of soluble iron and manganese (both in the +2 oxidation state), and at greater depth, sulfate reduction. Denitrification was confirmed by isotopic studies; nitrogen-15 is enriched (up to 100 permil) in low-nitrate groundwater at intermediate depths. Ammoniam-N in water also is present at concentrations as high as 26 mg/L (Schroeder et al., 1993). It is postulated that if new analytical methods become available, similar isotopic data for selenium (80 : 76 mass ratios) will confirm microbial selenate reduction in the groundwater.

Groundwater in the Coachella Valley north of the Salton Sea has long been an important source of municipal and domestic supplies. Recharge is from precipitation in the high mountains north of the valley and also from imported Colorado River and northern California water. Groundwater that is suitable for human consumption also is found in the sparsely populated areas west and east of the irrigated low-lying central part of the Imperial Valley. Recharge is from local precipitation in the surrounding mountains, from the Colorado River, and from Colorado River underflow (on the east side of the valley).

III. EFFECTS ON BIOTA

The Salton Sea area has become an increasingly important habitat for resident fish and wildlife and for migratory waterfowl on the Pacific Flyway as wetland acreage in California has decreased. More than 90% of California's wetlands have been lost to other uses in the last 150 years, mostly to agricultural development in the Central Valley ('J. Bennett, personal communication, 1996). Almost 400 bird species have been documented to date, and more than a million individual birds use the Salton Sea area annually. The area also contains several endangered species, including the desert pupfish (*Cyprinodon macularius*), the Yuma clapper rail (*Rallus longirostris yumanensis*), and the brown pelican (*Pelecanus occidentalis*). Based on information from other areas, selenium concentrations are high enough in the wildlife of the Salton Sea area to present some hazard to reproductive success.

Selenium bioaccumulation in lower trophic organisms and biomagnification in the food chain causes highest residues to occur in the upper trophic levels. Bioaccumulation and biomagnification are apparent in rivers and drains (Fig. 4) and in the Salton Sea itself (Fig. 5) (Schroeder et al., 1993; Setmire et al., 1993). The figures show that concentrations at the highest freshwater trophic level are only half those in the highest trophic level in the Salton Sea. Selenium concentrations in these upper food chain sources represent a possible threat to the long-term survival of fish-eating birds feeding in the Salton Sea area, especially those feeding on fish from the Salton Sea. The shaded areas in Figures 4 and 5 represent a level of concern where selenium concentrations are elevated above background levels but rarely cause discernible adverse effects. High selenium concentrations

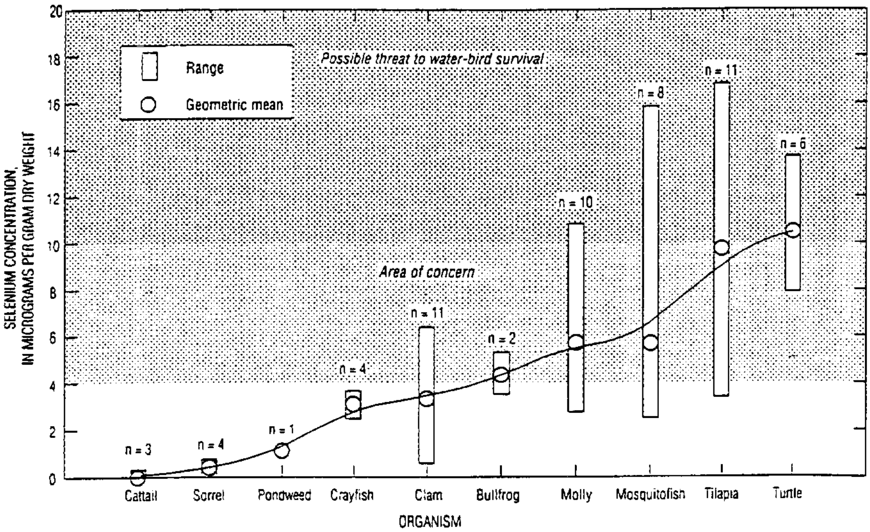

FIGURE 4 Concentration of selenium, and dietary thresholds, in food chain organisms of rivers and drains in the Imperial Valley, California 1988–1990: light shaded area, thresholds for area of concern; darker shaded area, possible threat to waterbird survival. (Modified from Heinz et al., 1987, 1989.)

also have been responsible for a California State Office of Health and Hazardous Assessment advisory limiting the consumption of fish caught in the Salton Sea to 113 g per 2-week period and prohibiting consumption altogether for pregnant women.

Livers from 145 individuals representing 10 waterfowl species were analyzed in the 1988–1990 study, and 10 (about 7%) of the samples were found to have concentrations exceeding the 30 μg/g dry weight threshold that indicates heavy exposure and a high risk of reproductive impairment (U.S. Fish and Wildlife Service, 1990; J. Skorupa, personal communication, 1992). More than 100 eggs of black-necked stilt (*Himantopus mexicanus*), a resident shorebird species, also were analyzed and only about 7% were found to exceed the 6 μg/g selenium threshold that predicts a 10% probability of embryotoxicity (death or deformity). Because of the low percentages, the likelihood of detecting teratogenesis, such as embryo and developmental abnormalities characteristic of classical selenium responses, is extremely low.

Additional data were collected by the U.S. Fish and Wildlife Service in 1992–1994 to further quantify biological effects of selenium on biota: 38 stilt eggs in 1992 and 40 additional stilt eggs in 1993. The geometric mean selenium

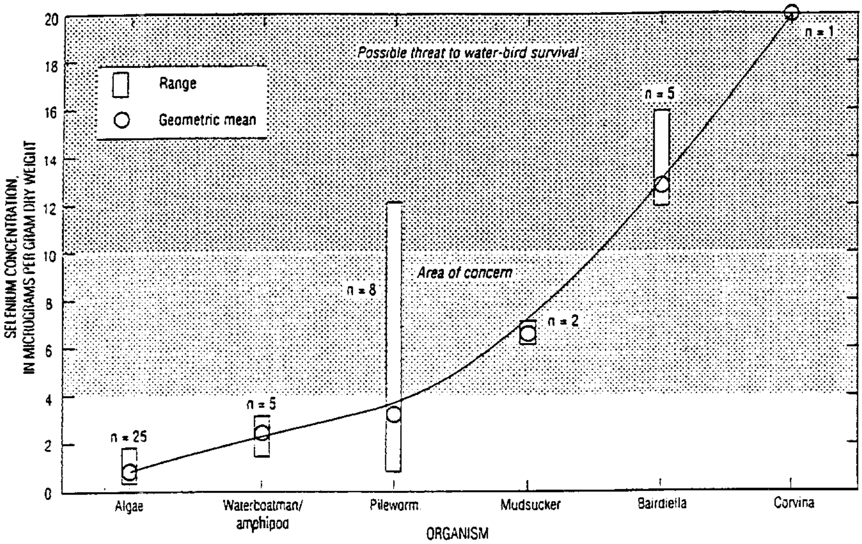

FIGURE 5 Concentration of selenium and dietary thresholds in food chain organisms of the Salton Sea, 1988–1990: light shaded area, thresholds for area of concern; darker shaded area, possible threat to waterbird survival. (Modified from Heinz et al., 1987, 1989.)

concentrations of 7 and 6 μg/g, respectively, are similar to those obtained during the 1988 to 1990 study (J. Bennett, personal communication, 1996).

Toxicological relationships established from studies in other areas, especially from the San Joaquin Valley, show that 15% of Salton Sea stilt nests were expected to be affected by hatching failure—close to the 13% that was actually observed (J. Skorupa, personal communication, 1994). Normally, about 8% of stilt nests with less than 4.1 μg/g selenium in their eggs have one or more fail-to-hatch eggs; hence there is only about a 5% reproductive depression in the Salton Sea area (J. Bennett, personal communication, 1996).

In addition to studies on waterfowl, sailfin mollies (*Poecilia latipinna*) were collected from 13 drains in 1994 to represent chemical body burdens of the endangered desert pupfish. The selenium levels in 1994 were found to be about the same as those in five mollies and four mosquitofish collected for the 1988–1990 study (Schroeder et al., 1993). For 10 of the 13 drains, selenium concentrations were in the range of 3 to 6 μg/g dry weight for whole-body fish, identified as a level of concern for warm-water fish (J. Bennett, personal communication, 1996). Mollies from two other drains had concentrations exceeding the toxicity threshold of 6 μg/g, above which there is increased risk of teratogenesis and embryo mortality (J. Bennett, personal communication, 1996).

IV. SUMMARY

Selenium is elevated in water, sediment, and biota in the Salton Sea area of California. Selenium in Colorado River water used for irrigation in the Imperial Valley has an average concentration of 2 μg/L. Irrigation drainwater in the Alamo River at its outlet to the Salton Sea has a median selenium concentration of 8 μg/L. Overall, selenium concentrations increase fourfold as a result of irrigated agriculture. Subsurface drainwater in the Imperial Valley had a median selenium concentration of 25 μg/L for 119 samples collected in May 1988 and 28 μg/L for 304 samples collected from August 1994 to January 1995, a 12- to 14-fold increase from the concentrations in the Colorado River. Ratios of selenium to chloride and comparisons between selenium concentrations in fields and in bottom sediments indicate that some selenium likely is lost to the bottom sediments of the surface drains. The Salton Sea, with a very low Se/Cl ratio, is a major sink for selenium, with only 1 μg/L selenium in the water column of the sea compared to the median of 8 μg/L selenium in the inflowing water of the Alamo River. Selenium contents in biota of the rivers and drains and in the Salton Sea also are elevated and are at levels of concern. Selenium bioaccumulates in food chain organisms and biomagnifies from lower to higher trophic levels. At greatest risk of reproductive impairment are the larger piscivorous birds feeding on fish in the Salton Sea.

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